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PATENT SPECIFICATION

(11) 1 548 037

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(21) Application No. 37903/76 (22) Filed 13 Sept. 1976
(31) Convention Application No. 2 540 655
(32) Filed 12 Sept. 1975 in
(33) Fed. Rep. of Germany (DE)
(44) Complete Specification published 4 July 1979
(51) INT CL² C08K 5/19, 3/24, 5/04
(52) Index at acceptance
C3K 123 124 241 280 281 282 291 292 296 KA

(19)

(54) ANTISTATIC THERMOPLASTIC MOULDING COMPOSITIONS AND SHAPED ARTICLES MADE THEREFROM

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to thermoplastic moulding compositions and shaped articles made therefrom.

As is known, thermoplastics such as vinyl chloride polymers, polyolefins, chlorinated polyethylenes, elastomers, for example acrylonitrile/butadiene/styrene (ABS), methylmethacrylate/butadiene/styrene (MBS) or methylmethacrylate/ acrylonitrile/ butadiene/ styrene (MABS) polymers, are insulators and therefore tend to become highly electrostatically charged. This causes difficulties in the manufacture of shaped (moulded) articles therefrom, and, because of the high electric surface resistance of such articles, for example sheets, further problems occur in processing, for example because of poor travel in machines, or sparking. The accumulation of electrostatic charges on shaped articles which are in daily use is also disadvantageous since the articles are easily soiled because of their inherently high dust attraction.

In order to suppress undesirable effects of electrostatic charge, thermoplastic shaped articles have been treated with surfactants or hygroscopic substances to divert these electrostatic charges. Although such external application of antistatics succeeds in rendering the shaped articles conductive for a short time, a lasting effect cannot be achieved because the agents applied only superficially are of course wiped off on handling and on use of the articles.

Antistatics have been intermixed with (incorporated into) the thermoplastic compositions from which shaped articles are manufactured, so that a more durable effect of the agent is attained. In the paper of S. Riethmayer in Gummi, Asbest, Kunststoffe 1973, *2*, pp. 76—88; id. *4*, pp. 298—308; id. *5*, pp. 419—429 and id. *6*, pp. 506—512, numerous antistatics for incorporation into thermoplastics are described, e.g. quaternary ammonium salts, fatty acid partial esters of polyols (see German Offenlegungsschrift No. 1,927,677), polyethyleneglycol fatty acid esters, fatty alcohol polyglycol esters and similar compounds. However, this paper shows that a single antistatic agent alone does not solve all the problems arising. For example, fatty acid partial esters of polyols are readily soluble in plastics, especially in polyvinyl chloride (PVC), and therefore cause neither any turbidity in transparent moulding compositions nor a significant disturbance of the stabilisation. However, their antistatic actvity is very poor. As against that, quaternary ammonium salts have a better antistatic activity, but they have to be used in relatively large amounts, calculated on the plastic material, and this high proportion adversely affects thermostability, for example of mixtures of vinyl chloride polymers. Moreover, it causes processing troubles, for example in calendering, due to formation of deposits on the rolls or deterioration of the surface by smudging. Incorporated even in small amounts, many of them still hinder stabilisation, and in all cases the antistatic effect obtained with these salts is insufficient for practical use.

Attempts have therefore been made to increase the antistatic activity of a compound in a synergistic manner by concomittantly using another antistatic substance. Thus, for example, the antistatic activity of fatty alcohol polyglycol ethers in polyolefins may be increased by polyethyleneglycol fatty acid esters (see the above paper, p. 426, right column, last paragraph).

There is therefore a need to provide an antistatic mixture for thermoplastic materials

which has an increased activity as compared to the antistatics known individually and which simultaneously does not adversely affect to any significant extent the processing properties of the corresponding thermoplastic compositions and the useful properties of the shaped articles made therefrom.

We have found that good results may be achieved by incorporating into the plastic material a tricomponent mixture of a quaternary ammonium salt, a partial ester of a polyol and an organic acid, and an inorganic or organic compound containing an ammonium, alkali metal or alkaline earth metal ion.

By such mixtures, it is possible to increase the relatively good antistatic activity of quaternary ammonium salts in such a manner that a high antistatic effect is obtained with only very small amounts while simultaneously preventing any significant trouble in the processing of the corresponding plastics compositions.

The present invention provides an antistatic agent which consists of a mixture of

A. from 0.4 to 1.5 parts by weight of a quaternary ammonium salt containing at least one aliphatic radical, especially an alkyl radical, having more than 8 carbon atoms and being linked to the nitrogen atom either directly or via a functional group.

B. from 0.5 to 2.5 parts by weight of a partial ester of a polyol and an organic acid, and

C. from 0.1 to 1.5 parts by weight of an ammonium, alkali metal, or alkaline earth metal salt of an inorganic or organic acid, an alkali metal or alkaline earth metal hydroxide, or a fatty alcoholate, phenolate, or naphthenate of an alkali or alkaline earth metal.

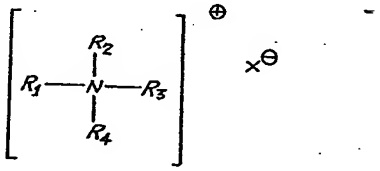
The present invention also provides an antistatic thermoplastic moulding composition which contains an antistatic agent of the present invention, and shaped articles made from such moulding compositions. In the moulding composition, component A is suitably present in an amount of from 0.4 to 1.5% by weight, component B in an amount of from 0.5 to 2.5% by weight, and component C in an amount of from 0.1 to 1.5% by weight, each relative to the total plastics mixture.

The present invention further provides a process for the manufacture of an antistatic thermoplastic moulding composition, which comprises intermixing the three components A, B and C with a powdery thermoplastics material.

It was surprising to observe that the antistatic agent of the present invention not only gives a very high antistatic effect, but also has nearly no adverse influence on the thermostability of, for example, stabilised vinyl chloride polymer compositions. Moreover, it is especially surprising that the partial esters, having *per se* an insignificant or very low antistatic activity, produce a considerable synergistic increase of the antistatic effect of quaternary ammonium salts in the case where an inorganic or organic compound containing an ammonium, alkali metal or alkaline earth metal ion is concomittantly used.

As quaternary ammonium salts (component A) there may be used in principle all those containing in the molecule at least one aliphatic radical, (straight-chain, branched and/or cyclic) having at least 8 carbon atoms and being linked to the nitrogen atom either directly or via functional groups, for example compounds obtained by quaternisation of corresponding amines or diamines such, for example, as primary, secondary or tertiary aliphatic or cycloaliphatic amines or diamines; of amides such, for example, as fatty acid amides or urea derivatives; or of nitrogen-containing heterocyclic compounds such, for example, as pyridine compounds or imidazolines. Quaternary ammonium salts of this kind and the methods of preparation thereof are for example described in detail in the Riethmayer paper cited above (pp. 298 to 304).

Advantageously, there is used a quaternary ammonium salt of the general formula



wherein

R_1 represents a linear, preferably saturated or mono-unsaturated aliphatic radical having more than 8 carbon atoms and advantageously less than 31 carbon atoms, preferably from 10 to 18 carbon atoms, especially a decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, stearyl, oleyl, coconut-alkyl or tallow-alkyl radical and being linked to the nitrogen atom either directly or preferably via an amino-N-alkyl, O-alkyl, N-alkyl or benzyl group, wherein "alkyl" denotes a radical having from 1 to 6 carbon atoms, optionally substituted by one or more hydroxy groups,

R_2 represents a hydrogen atom or an alkyl radical having from 1 to 18 carbon atoms, preferably from 1 to 6 carbon atoms, for example a methyl, ethyl, propyl or butyl radical, or a benzyl radical,

R_3 and R_4 which may be the same or different, each represents a linear, saturated or mono-unsaturated aliphatic radical having from 1 to 18 carbon atoms, a benzyl radical

or a radical of the formula

$$-(CH_2CH_2O)_nH$$

(n being in the range of from 1 to 30); or R_3 and R_4 may also form a ring having from 4 to 10, preferably from 4 to 6, carbon atoms, which may be saturated or unsaturated.

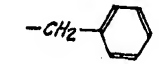
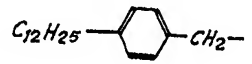
X represents a halogen, preferably chlorine or bromine, atom, or a perhalogenate anion, preferably ClO_4 or BrO_4, or NO_3, HSO_4 or CH_3SO_4.

A mixture of two or more quaternary ammonium salts may be used.

Table 1 lists preferred quaternary ammonium salts. Especially suitable are compounds containing the R_1 groups shown in Nos. 8, 9, 10, 12 and 13.

Table 1 demonstrates also the variety of suitable quaternary ammonium salts. The essential characteristics for the effect of such a salt resides in the fact that it contains an alkyl radical having more than 8 carbon atoms which is linked to the nitrogen atom either directly or via a functional group.

TABLE 1
Preferred quaternary ammonium salts

No. of compounds	R_1	R_2	R_3	R_4	X
1	$-C_{12}H_{25}$	$-CH_3$	$-CH_3$	$-CH_3$	Cl
2	$-C_{12}H_{25}$	$-CH_3$		$-CH_3$	Cl
3	$-C_{12}H_{25}$	$-CH_3$	$-CH_3$	$-CH_2CH_2OH$	HSO_4
4	$-C_{12}H_{25}$	$-CH_3$	$-CH_2CH_2OH$	$-CH_2CH_2OH$	CH_3SO_4
5		$-CH_3$	$-CH_3$	$-CH_2CH_2OH$	ClO_4
6	$-C_{16}H_{33}$	$-CH_3$	$-CH_3$	$-CH_3$	Br
7	$-C_{18}H_{37}$	$-CH_3$	$-C_{18}H_{37}$	$-CH_3$	Cl
8	* coconut alkyl	H	$-CH_2CH_2OH$	$-CH_2CH_2OH$	ClO_4
9	** tallow alkyl–N(CH_3)–$(CH_2)_3$– (CH_3)	$-CH_3$	$-CH_3$	$-CH_3$	2 CH_3SO_4
10	$C_{11}H_{23}C(=O)-NHCH_2-CH_2-$	$-CH_3$	$-CH_3$	$-CH_3$	CH_3SO_4
11	$C_{17}H_{33}C(=O)-NH(CH_2)_3-$	$-CH_3$	$-CH_3$	$-CH_2CH_2OH$	NO_3
12	$C_{12}H_{25}OCH_2CH(OH)CH_2-$	$-CH_3$	$-CH_2CH_2OH$	$-CH_2CH_2OH$	CH_3SO_4
13	$C_{14}H_{29}O(CH_2)_3-$	$-CH_3$	$-CH_2CH_2OH$	$-CH_2CH_2OH$	CH_3SO_4
14	tallow alkyl–$OCH_2CH(OH)CH_2-$	$-CH_3$	$-CH_2CH_2OH$	$-CH_2CH_2OH$	CH_3SO_4

Notes to Table 1.

* coconut alkyl corresponds to the following typical chain distribution: C_8: C_{10}: C_{12}: C_{14}: C_{16}: C_{18} in a proportion of 7:6:51:19:8:9, 50 to 80 % by weight of C_{18} being oleyl

** tallow alkyl corresponds to the following typical chain distribution: C_{14}: C_{16}: C_{18} in a proportion of 5:25:65, 50 % by weight of C_{18} being oleyl

In accordance with this invention, the quaternary ammonium salts or mixtures thereof are used in amounts of from 0.4 to 1.5% by weight, preferably from 0.5 to 1% by weight, relative to the total plastics mixture.

According to this invention, those partial esters of a polyol and an organic acid are advantageously used which have at least one free hydroxy group and which are of liquid to pasty consistency because of their low esterification degree, since in this state they are easily and homogeneously incorporated into the plastics composition.

A mixture of two or more partial esters may be used.

Suitable are for example partial esters of a polyol and a fatty acid or a fatty acid mixture having from 6 to 25 carbon atoms. Preferred are partial esters of a polyol having from 2 to 6 carbon atoms, especially ethyleneglycol, glycerol, diglycerol, erythritol, pentaerythritol, pentitol, or hexitol, or an oxyethylate or oxypropylate of these polyols and a fatty acid or fatty acid mixture having from 6 to 18 carbon atoms, preferably capronic, caprylic, capric, lauric, palmitic, stearic, oleic or ricinoleic acid or mixtures of these acids, preferably a capronic/capric acid mixture, in a 1:1 ratio, a coconut or tallow fatty acid (composition of these two acids see Table 1). Particularly advantageous are monoglycerides, diglycerides or monosorbitols of the above individual fatty acids or fatty acid mixtures, especially glycerol monooleate, glycerol monoricinoleate, glycerol monococoate, glycerol monoester of a capronic/capric acid mixture in a 1:1 ratio, diglycerol monooleate or monococoate and sorbitan monolaurate.

The preparation of the partial esters is described for example in the cited Riethmayer paper or in the German Offenlegungsschrift No. 1,927,677 also mentioned above.

The partial ester or mixture thereof is suitably used in an amount of from 0.5 to 2.5% by weight, preferably from 1 to 1.5% by weight, relative to the total plastics mixture.

As component C, there are advantageously used ammonium, alkali metal or alkaline earth metal salts of inorganic or organic acids, for example salts of boric, perboric, carbonic, phosphoric, phosphorous, silicic acid or of fatty acids, optionally epoxidized, having from 6 to 25, preferably from 10 to 18, carbon atoms, furthermore alkali metal or alkaline earth metal hydroxides such as calcium or barium hydroxide, fatty alcoholates, phenolates or naphthenates of alkali or alkaline earth metals or a mixture of two or more such compounds. Especially suitable are calcium carbonate (precipitated chalk), sodium carbonate (soda) and barium or calcium soaps such as barium or calcium salts of lauric, palmitic, stearic, oleic or ricinoleic acid.

Of course, the use of compounds being known for causing a catalytic decomposition of the thermoplastic material or of its stabilizer must be avoided.

It is especially advantageous to use as component C those compounds which simultaneously are lubricants for the plastics material used. Thus, in the case where the plastic material is a vinyl chloride polymer, the above soaps, preferably calcium palmitate or stearate, or calcium montanate or OP wax (1,3-butanediol-montanic acid ester chalked, so that about 40 of the initially used montanic acid is present in the form of calcium salt), known as good lubricants are particularly appropriate.

According to this invention, the inorganic or organic compound having an ammonium, alkali metal or alkaline earth metal ion, or mixture thereof is suitably used in an amount of from 0.1 to 1.5% by weight, preferably from 0.1 to 0.5% by weight, relative to the total plastics mixture. In the case where the compound employed is simultaneously a lubricant for the plastic material, it is advantageous to use an amount of about the indicated upper limit, while in all other cases an amount near the inferior limit is recommended.

The antistatic agent according to the present invention is suitable preferably for vinyl chloride homo- and copolymers or graft copolymers having a content of at least 50% by weight, preferably 75% by weight, and especially 85% by weight of polymerizable vinyl chloride, relative to the total polymer.

The following monomers are suitable, for example, for being copolymerized with vinyl chloride: olefins such as ethylene or propylene, vinyl esters of straight-chain or branched carboxylic acids having from 2 to 20, prefer-

ably from 2 to 4 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl-2-ethylhexoate, vinyl stearate; vinylic halides, such as vinyl fluoride, vinylidene fluoride, vinylidene chloride; vinyl ethers, unsaturated acids, such as maleic acid, fumaric acid, acrylic acid, methacrylic acid and their monoesters or diesters with monoalcohols or dialcohols having from 1 to 10 carbon atoms; acrylonitrile, styrene, and cyclohexyl maleimide.

For carrying out graft polymerization there may be used, for example, elastomeric polymerizates which have been obtained by polymerizing one or more of the following monomers: dienes, such as butadiene and cyclopentadiene; olefins, such as ethylene, propylene; styrene, unsaturated acids, such as acrylic acid or methacrylic acid, as well as their esters with monoalcohols or dialcohols having from 1 to 10 carbon atoms, acrylonitrile, vinyl compounds, such as vinyl esters of straight chained or branched carboxylic acids having from 2 to 20, preferably from 2 to 4 carbon atoms, vinyl halides, such as vinyl chloride and vinylidene chloride. Mixtures of the cited polymers may also be employed.

The antistatic agent in accordance with this invention is particularly suitable for the above vinyl chloride polymers or mixtures thereof with each other or with other polymers, preferably with ABS, MBS, MABS polymers, chlorinated polyethylene or ethylene/vinyl acetate copolymers; the vinyl chloride polymer proportion being quantitatively preponderant.

The molding composition of the invention, besides the tricomponent antistatic agent, may contain advantageously processing auxiliaries and optionally one or more other special additives such as heat and light stabilizers, lubricants, plasticizers, pigments or optical brighteners.

Suitable heat and light stabilizers are, for example, monoalkyl tin compounds and dialkyl tin compounds, the alkyl radicals having from 1 to 10 carbon atoms, the remaining valencies of the tin contained in these compounds being bound with further substituents by means of oxygen and/or sulfur atoms; aminocrotonic acid esters, urea and thiourea-derivatives such as monophenyl urea and diphenyl thiourea, α-phenylindole. Organo-tin/sulfur stabilizers such as dimethyl - tin - bis(2-ethylhexyl-thioglycolate), di - n - butyl - tin - bis(2-ethylhexyl - thioglycolate), or di - n - octyl-tin - bis - (2 - ethylhexyl - thioglycolate) are preferred.

The stabilizers are suitably employed in quantities of from 0.2 to 3 weight %, calculated on the total mixture; they may be used as mixtures with each other and with antioxidants, such as alkyl-substituted hydroxyl compounds, for example ditertiary butyl paracresol, dibutylhydroxy-naphthalene, tertiary butylhydroxy anisole, and organo-phosphorus acid esters, e.g. tris-(mono- or di)-nonylphenyl phosphite. The light stability may be improved by adding to the mixtures UV-light absorbing substances, such as derivatives of benzophenone or benzotriazole, e.g. 2 - (2'-hydroxy - 5' - methylphenyl)benzotriazole or 2 - (2' - hydroxy - 3' - tertiary butyl - 5'-methylphenyl) - 5 - chloro - benzotriazole.

As lubricants there may be used, for example, one or more higher aliphatic carboxylic acids or hydroxycarboxylic acids, as well as their esters and amides, such as stearic acid, montanic acid, bis-stearyl- or bis-palmitoyl-ethylene diamine, montanic acid ester of ethanediol or 1,3-butanediol, fatty alcohols having more than 10 carbon atoms, and their ethers, low-molecular polyolefins, hard paraffins. A mixture of two or more lubricants may be used. The lubricant component is suitably used in amounts of from 0.1 to 1.5 weight %, calculated on the total mixture.

As plasticizers there may be employed for example one or more esters of aromatic or aliphatic dicarboxylic or tricarboxylic acids, of higher alkylsulfonic acids and of phosphoric acid, such as di - 2 - ethyl - hexyl-phthalate, di - 2 - ethylhexyl - adipate or -sebacate, alkylsulfonic acid ester of phenol or cresol, tricresyl-phosphate, epoxidized soja oils or castor oils. A mixture of two or more plasticizers may be used. Preferred are, however, plasticizer-free mixtures.

In order to incorporate the antistatic agent in accordance with this invention, the processing agents and optionally special additives into the plastics powder, the components are thoroughly and homogeneously mixed. For this purpose, usual blending equipment may be employed, advantageously a high-speed mixer (fluid mixer). It is advantageous to carry out the homogenization in a heating/cooling mixer equipment usual in plastics processing, where the mixture is heated in the high-speed mixer to a temperature of about 140°C by means of the agitation energy, thus ensuring a homogeneous intermixing of the individual components, and subsequently it is cooled in the cooling mixer.

Processing (molding) of the molding compositions of this invention is carried out according to known methods of thermoplastics manufacture, for example extrusion, calendering, injection molding, compression molding or blow molding of hollow articles.

The molding compositions of the invention are appropriate for the manufacture of all those shaped articles for which good and lasting antistatic properties are desired, preferably the manufacture of transparent sheets having an antistatic finish from plastics on the

basis of vinyl chloride polymers by means of calendering or extrusion. In the case of calendering, the mixtures may be pregelled at about 140° C on a plastifying apparatus such as kneader or mixing roll, and subsequently processed to sheets on a two- or multiple-roll calender, advantageously on a four- or five-roll calender, at a temperature of the rolls of about 190 to about 210°C.

The following examples illustrate the invention. In all cases, a vinyl chloride suspension homopolymer (S-PVC) having a K value of 60 (according to German Industrial Standard DIN 53 726) and heat-stabilized by di - n - butyl - tin - bis - 2 - ethylhexyl-thioglycolate was used.

The mixing components of the individual examples which are listed in Table 2 are blended in a high-speed mixer. At first, the thermostability is determined in the roll test using a small portion of the above mixture. The remainder is pregelled at 140° C on a kneader and calendered on a four-roll calender the rolls of which are heated at 190°, 195°, 200° and 210° C (in travelling direction of the material) to form a sheet having a thickness of 150µm. The antistatic effect of the sheet is subsequently tested, that is, its surface resistance is measured in ohms (R_{OA}) according to German Industrial Standard DIN 53 482, using a digital Thera ohmmeter of Messrs. Kamphausen at a test voltage of 100 volts, its electrostatic charge in volts/cm according to German Industrial Standard DIN 53 486 and the half-value time in minutes or seconds also according to DIN 53 486. Instead of the friction device according to DIN 53 486 for applying an electric charge to the sheet test specimens, a point discharge device (Korona) having 9 kilovolts is used in order to apply the charge without contact.

Before measuring, the test specimens are stored for 24 hours in normal climate 24/50 (i.e. 23 ± 2° C and 50 ± 5% of relative humidity) according to German Industrial Standard DIN 50 014.

The thermostability of the mixture is determined according to the roll test method as follows: about 300 g of the corresponding mixture are charged to a two-roll mill (dimensions of rolls: length about 40 cm. diameter about 15 cm) the rolls of which are heated at 180° C and make about 18 and 20 rpm, and laminated to a sheet. The time (minutes) which passes until a distinct yellowing occurs is measured, the resulting minutes determine the thermostability of the corresponding mixture.

Besides the starting mixtures, also the test results are listed in Table 2, that is, the thermostability of the mixture in minutes, the surface resistance (R_{OA}) in ohms, the charge in volts/cm and the half-value time in minutes or seconds, the latter three of the sheets manufactured from the mixtures.

The quaternary ammonium salt used in the corresponding starting mixture is one of the compounds listed in Table 1; the "mixing components" column of Table 2 contains therefore the numbers of the corresponding salts according to Table 1. Furthermore, the known abbrevations "wax OP" (for 1,3-butanediolmontanic acid ester chalked, so that about 40% of the initially used montanic acid are present in the form of calcium salt), "wax E" (for 1,3-butanediolmontanic acid ester) and "wax C" (for bis-stearylethylene diamine) are used.

The amounts of the mixing components are indicated in % by weight.

TABLE 2
Survey of Examples

Example No.	Mixing components	R_{OA} ohms	Charge volts/cm	Half-value time min. (') or sec. (")	Thermostability min (')
Comparative Examples					
1	88.1 S–PVC 10.0 MABS 1.5 butyl-tin 0.4 wax OP	10^{14}	4100	more than 30'	40'
2	87.1 S–PVC 10.0 MABS 1.5 butyl-tin 0.4 wax OP 1.0 glycerol monooleate	10^{12}	3600	more than 30'	40'
3	87.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.4 wax E 0.5 No. 12	10^{13}	3800	more than 30'	40'
4	87.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.4 wax OP 0.5 No. 12	10^{10}	3500	3,1'	30'

TABLE 2 (Continued)

Example No.	Mixing components	R_{OA} ohms	Charge volts/cm	Half-value time min. (') or sec. (")	Thermostability min. (')
Examples in accordance with the invention					
5	86.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.2 wax E 0.5 No. 12 1.0 glycerol monooleate 0.2 Ca-stearate	10^9	2600	25"	30'
6	96.6 S–PVC 1.5 butyl-tin 0.5 No. 12 1.0 glycerol monooleate 0.4 Ca-stearate	10^9	3000	30"	35'
7	96.6 S–PVC 1.5 butyl-tin 0.5 No. 12 1.0 glycerol monooleate 0.4 wax OP	10^9	2200	25"	35'
8	96.2 S–PVC 1.5 butyl-tin 0.4 wax E 0.5 No. 12 1.0 glycerol monooleate 0.4 $CaCO_3$ (chalk)	10^9	3000	30"	35'

TABLE 2 (Continued)

Example No.	Mixing components	R_{OA} ohms	Charge volts/cm	Half-value time min. (') or sec. (")	Thermostability min. (')
Examples in accordance with the invention					
9	96.2 S–PVC 1.5 butyl-tin 0.4 wax C 0.5 No. 12 1.0 glycerol monooleate 0.4 $CaCO_3$ (chalk)	10^8	3000	10"	25'
10	86.1 S–PVC 10.0 MABS 1.5 butyl-tin 0.4 wax E 0.5 No. 12 1.0 glycerol monooleate 0.4 $NaCO_3$ (soda)	10^8	1250	5"	35'
11	84.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.5 No. 12 1.0 glycerol monoricinoleate 0.4 wax OP	10^9	2700	40"	40'
12	86.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.5 No. 12 1.0 diglycerol monooleate 0.4 wax OP	10^9	2600	25"	35'

TABLE 2 (Continued)

Example No.	Mixing components	R_{OA} ohms	Charge volts/cm	Half-value time min. (') or sec. (")	Thermostability min. (')
Examples in accordance with the invention					
13	86.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.5 No. 12 1.0 glycerol monococoate 0.4 wax OP	10^9	2400	25"	35'
14	86.3 S–PVC 10.0 MABS 1.5 butyl-tin 0.8 No. 9 1.0 glycerol monooleate 0.4 wax OP	10^8	2800	30"	30'
15	86.5 S–PVC 10.0 MABS 1.5 butyl-tin 0.6 No. 9 1.0 glycerol monoester of capronic/capric acid (1:1) 0.4 wax OP	10^8	3400	15"	35'
16	86.5 S–PVC 10.0 MABS 1.5 butyl-tin 0.6 No. 10 1.0 glycerol monooleate 0.4 wax OP	10^8	1800	10"	25'

TABLE 2 (Continued)

Example No.	Mixing components	R_{OA} ohms	Charge volts/cm	Half-value time min. (') or sec. (")	Thermostability min. (')
Examples in accordance with the invention					
17	86.1 S–PVC 10.0 MABS 1.5 butyl-tin 0.4 wax E 0.6 No. 8 1.0 glycerol monooleate 0.4 $NaCO_3$ (soda)	10^9	3000	30"	40'
18	86.5 S–PVC 10.0 MABS 1.5 butyl-tin 0.6 No. 9 1.0 glycerol monoester of capronic/capric acid (1:1) 0.4 wax OP	10^8	3400	15"	30'
19	86.6 S–PVC 10.0 chlorinated poly-ethylene (Cl content 39 %) 1.5 butyl-tin 0.5 No.13 1.0 glycerol monooleate 0.4 wax OP	10^9	1600	15"	35'
20	86.6 S–PVC 10.0 MABS 1.5 butyl-tin 0.5 No. 13 1.0 glycerol monoester of capronic/capric acid (1:1) 0.4 wax OP	10^9	2000	10"	35'

Further explanations as to the preceding Examples are given as follows:

Comparative Example 1 is a usual formulation on the basis of a vinyl chloride polymer, which contains wax OP (component C) as lubricant.

The molding composition or sheet of Comparative Example 2 contains glycerol monooleate (component B) besides wax OP (component C).

In Comparative Example 3, a quaternary ammonium salt (component A) is present, wax E serving as lubricant.

Besides wax OP (component C), the molding composition or sheet of Comparative Example 4 contains also a quaternary ammonium salt (component A).

Examples 5 through 20 are molding compositions or shaped articles according to this invention. As results from Table 2, they have a particularly high antistatic effect, and above all, they are distinguished by the fact that this antistatic effect is obtained with the use of extremely small quantities, resulting in the following further advantages:

The thermostability of the molding compositions is maintained, especially in view of ensuring a trouble-free processing on an industrial scale.

No substantial problems arise during the different processing steps such as mixing, calendering or extrusion, above all there is no substantial formation of deposits on machine parts (nozzles, rolls), no substantial smudging and thus no substantial surface deterioration of the manufactured shaped articles.

Furthermore, the properties inherent in the molding compositions and shaped articles, for example transparency, strength, tenacity, hardness, heat resistance, are substantially maintained.

A substantial advantage of the sheets having an antistatic finish in accordance with this invention resides in the fact that this antistatic finish does not substantially adversely affect further processing of the sheets, for example deep-drawing to articles of daily use, compression molding to audiovisual information carriers, or the application of such sheets in the packaging field. Especially, there is no substantial settling of deposits or residues in the corresponding processing machines (deep-drawing equipment, presses), and the finished articles obtained do not show any substantial surface deterioration, caused for example by exudation.

WHAT WE CLAIM IS:—

1. An antistatic agent which consists of a mixture of

A. from 0.4 to 1.5 parts by weight of a quaternary ammonium salt containing at least one aliphatic radical having more than 8 carbon atoms and being linked to the nitrogen atom either directly or via a functional group,

B. from 0.5 to 2.5 parts by weight of a partial ester of a polyol and an organic acid, and

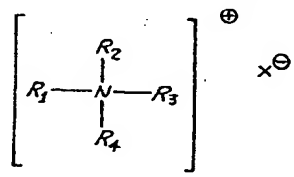
C. from 0.1 to 1.5 parts by weight of an ammonium, alkali metal or alkaline earth metal salt of an inorganic or organic acid, an alkali metal or alkaline earth metal hydroxide or a fatty alcoholate, phenolate, or naphthenate of an alkali or alkaline earth metal.

2. An antistatic agent as claimed in claim 1, which contains from 0.5 to 1 parts by weight of component A.

3. An antistatic agent as claimed in claim 1 or claim 2, which contains from 1 to 1.5 parts by weight of component B.

4. An antistatic agent as claimed in any one of claims 1 to 3, which contains from 0.1 to 0.5 parts by weight of component C.

5. An antistatic agent as claimed in any one of claims 1 to 4, wherein component A comprises a compound of the general formula



wherein

R_1 represents a linear, saturated or mono-unsaturated aliphatic radical having more than 8 carbon atoms, and being linked to the nitrogen atom either directly or via an amido-N-alkyl, O-alkyl, N-alkyl or benzyl group; wherein "alkyl" denotes a radical having from 1 to 6 carbon atoms which is unsubstituted or substituted by one or more hydroxy groups,

R_2 represents a hydrogen atom, an alkyl radical having from 1 to 18 carbon atoms or a benzyl radical;

R_3 and R_4, which may be the same or different, each represents a linear, saturated or mono-unsaturated aliphatic radical having from 1 to 18 carbon atoms, a benzyl radical or a radical of the formula

$$-(CH_2CH_2O)_nH$$

wherein n represents an integer from 1 to 30, or R_3 and R_4 together represent a bivalent saturated or mono-unsaturated aliphatic radical having from 4 to 10 carbon atoms; and

X represents a chlorine or bromine atom or ClO_4, BrO_4, NO_3, HSO_4 or CH_3SO_4.

6. An antistatic agent as claimed in claim 5, wherein the aliphatic radical represented by R_1 has not more than 31 carbon atoms.

7. An antistatic agent as claimed in claim 6, wherein the aliphatic radical represented by

R_1 has from 10 to 18 carbon atoms.

8. An antistatic agent as claimed in any one of claims 5 to 7, wherein the alkyl radical represented by R_2 has from 1 to 6 carbon atoms.

9. An antistatic agent as claimed in any one of claims 5 to 8, wherein the bivalent aliphatic radical represented by R_3 and R_4 has from 4 to 6 carbon atoms.

10. An antistatic agent as claimed in any one of claims 1 to 4, wherein component A is any one of those specified in Table 1 herein.

11. An antistatic agent as claimed in claim 10, wherein component A is the compound listed as number 8, 9, 10, 12 or 13 in Table 1 herein.

12. An antistatic agent as claimed in any one of claims 1 to 11, wherein component B comprises a partial ester of a polyol having from 1 to 6 carbon atoms and a fatty acid or a fatty acid mixture having from 6 to 18 carbon atoms.

13. An antistatic agent as claimed in claim 12, wherein component B comprises glycerol monooleate, glycerol monoricinoleate, glycerol monococoate, glycerol monoester of a capronic/capric acid mixture in a substantially 1:1 ratio, diglycerol monooleate or monococoate or sorbitan monolaurate.

14. An antistatic agent as claimed in any one of claims 1 to 13, wherein component C comprises an ammonium, alkali metal or alkaline earth metal salt of carbonic acid, an alkali metal or alkaline earth metal hydroxide or an alkali metal or alkaline earth metal soap.

15. An antistatic agent as claimed in claim 14, wherein component C comprises calcium carbonate, sodium carbonate or the barium or calcium salt of lauric, palmitic, stearic, oleic or ricinoleic acid or calcium montanate, or OP wax.

16. An antistatic agent as claimed in claim 15, wherein component C comprises a lubricant.

17. An antistatic agent as claimed in claim 1, which is substantially as described in any one of the Examples herein.

18. An antistatic thermoplastic moulding composition which comprises

I. a thermoplastic polymer and

II. an antistatic agent, which consists of a mixture of the following three components:

A. a quaternary ammonium salt containing at least one aliphatic radical having more than 8 carbon atoms and being linked to the nitrogen atom either directly or via a functional group,

B. a partial ester of a polyol and an organic acid, and

C. an ammonium, alkali metal, or alkaline earth metal salt of an inorganic or organic acid, an alkali metal or alkaline earth hydroxide or a fatty alcoholate, phenolate, or naphthenate of an alkali or alkaline earth metal;

component A being present in an amount of from 0.4 to 1.5% by weight, component B in an amount of from 0.5 to 2.5% by weight, and component C in an amount of from 0.1 to 1.5% by weight, each percentage being relative to the total plastics mixture.

19. A moulding composition as claimed in claim 18, which contains from 0.5 to 1% by weight of component A.

20. A moulding composition as claimed in claim 18 or claim 19, which contains from 1 to 5% by weight of component B.

21. A moulding composition as claimed in any one of claims 18 to 20, which contains from 0.1 to 0.5% by weight of component C.

22. A moulding composition as claimed in claim 18, wherein component A is present in an amount of from 0.5 to 1% by weight, component B in an amount of from 1 to 1.5% by weight, and component C in an amount of from 0.1 to 0.5% by weight, each relative to the total plastics mixture.

23. A moulding composition as claimed in any one of claims 18 to 23, wherein the antistatic agent is as specified in any one of claims 7 to 19.

24. A moulding composition as claimed in any one of claims 18 to 23, wherein component I comprises a vinyl chloride polymer.

25. A moulding composition as claimed in claim 24, wherein component I includes a minor proportion of ABS, MBS or MABS resin, chlorinated polyethylene or ethylene/vinyl acetate copolymer.

26. A moulding composition as claimed in any one of claims 18 to 25, which contains one or more additives selected from heat and light stabilisers, lubricants, plasticisers, pigments, optical brighteners and impact strength modifiers.

27. A moulding composition as claimed in claim 18, substantially as described in any one of the Examples herein.

28. A shaped article manufactured from a moulding composition as claimed in any one of claims 18 to 27.

29. A process for the manufacture of a shaped article, which comprises intermixing an antistatic agent as claimed in any one of claims 1 to 17 with a powdery thermoplastics material and processing this mixture to a shaped article according to a known process.

30. A process as claimed in claim 29, wherein the thermoplastic material comprises a vinyl chloride polymer and one or more processing auxiliaries selected from stabilisers, lubricants and impact strength modifying agents, is added to the moulding composition before processing.

31. A shaped article whenever manufactured by a process as claimed in claim 29 or claim 30.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.